61914

Reg. No. [ ][ ][ ][ ][ ][ ][ ][ ]

II Semester M.Sc. Degree Examination, November – 2022
CHEMISTRY
Molecular Spectroscopy-I
(CBCS Scheme 2019-20)
Paper : Ch - 204

Time : 3 Hours   Maximum Marks : 70

Instructions to Candidates:

Answer question **No.1** and any **Five** of the remaining questions. Figures to the right indicate marks.

Answer any **Ten** of the following.   (10×2=20)

1. a) Define the term "point group" and find the point group of tetrahedral CH_3Cl Molecule.

    b) What do the Mulliken symbols B_{1g} and A_{2u} signify?

    c) List the sub-group of D_{3h} point group. Give the order of each sub-group.

    d) Acetylene has the two following C-H vibrations, a symmetrical one at 3287 cm^{-1} and unsymmetrical one at 3374 cm^{-1}, $\overleftrightarrow{H-C}=\overleftrightarrow{C-H}$ and $\overleftrightarrow{H-C}=C=\overleftrightarrow{H}$. Which of the vibration will be Raman active? Why?

    e) Calculate the number of normal modes of vibrations of, N_2O and CO_2 molecules.

    f) Calculate force constant for a harmonic spring exhibiting vibrational frequency of 10s^{-1} for a mass of 1kg.

    g) CO_2 does not show its pure rotational spectrum but does show rotation-vibration spectrum. Give reasons.

    h) How rotational energy of linear molecule differs from that of symmetric top molecule? Explain.

    i) The spacing between successive lines in the rotational Raman spectrum of a diatomic molecule is 12 cm^{-1}. What is the Raman shift of the first stokes line?

    j) With the help of Jablonski diagram indicate the transitions responsible for fluorescence and phosphorescence.

    k) Write the electronic structure of O_2 and calculate the bond order.

                                                                    [P.T.O

1) State and explain Born-Oppenheimer approximation.

2. a) List the diagnostic symmetry elements and determine the point group symmetries of the following molecules:

   i) C_3H_4 (allene)

   ii) BF_3

   iii) $[PtCl_4]^{2-}$

   iv) CH_2Cl_2 and

   v) C_2H_4 (5+5=10)

   b) Construct the Multiplication table for the symmetry operations of ammonia molecule.

3. a) Deduce the matrix representation for rotation of a vector with respect to Z-axis and evaluate the matrix for C_2 and C_3 operations.   (6+4=10)

   b) Show that two σ_v - operations of C_{2v} point group are non-conjugate while that of three σ_{v-} Operations of C_{3v} are conjugate.

4. a) Derive an expression for the spectral frequency for vibration-rotation spectra of diatomic molecules. Comment on the effect of interaction between vibration and rotational energies on rotational lines.   (4+6=10)

   b) Write brief notes on.

   i) Parallel and perpendicular vibrations.

   ii) Time dependent perturbation theory.

5. a) $H^{35}Cl$ has a B value of 10.593 cm^{-1} and a centrifugal distortion constant of 5.3×10^{-4} cm^{-1}. Estimate the vibrational frequency and force constant of the molecule.   (5+5=10)

   b) Depict the normal modes of XY_2 linear and non-linear type molecules and explain their IR activity.

6. a) Calculate the rotational energy of $^{14}N^{16}O$ corresponding to J=1 level in joules and in cm^{-1}. Assuming it to be rigid rotator (Given atomic masses of ^{16}O=15.9994 amu and ^{14}N=14.004 amu and the bond length is 115 pm).   (4+6=10)

b) Write short notes on:

   i)   Q-branch in vibration-rotation spectra and

   ii) FT-IR spectrometer.

7. a) How do you account for the difference in intensities of Stokes and anti-Stokes lines from quantum theory of Raman spectra? **(4+6=10)**

   b) Explain how IR and Raman spectrum of molecules are complementary to each other. With an illustrative example discuss their combined application in structural elucidation.

8. a) Explain the importance of Frank-Condon principle for explaining the intensities of vibrational structure. **(5+5=10)**

   b) Write the molecular orbital diagram of formaldehyde molecule and explain the possible electronic transitions involved in it.